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Peculiarities of charged domain walls and local polarization reversal in β-glycine single crystals

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Currently, inorganic ferroelectrics are widely used as efficient piezoelectrics, pyroelectrics, memory cells, and electrooptic modulators [1], but they are not biologically compatible and require encapsulation for contact with biological environment. In this context, piezoelectric or pyroelectric materials made from the building blocks used by nature may be used. Recent studies revealed that the softness of hydrogen bonds in some classes of biomolecular polar materials may be the origin of strong piezoelectric and pyroelectric properties at room temperature [2]. It was recently shown that the peculiar molecular packing in amino acids may give rise to the strong piezoelectric response, as exemplified by glycine [3]. Glycine is the simplest amino acid and is polymorphic in nature being ferroelectric in its polar β-phase [4]. Its strong piezoelectricity and ability to switch polarization under the action of electric field adds new functionality that can be further used in biomedical applications.

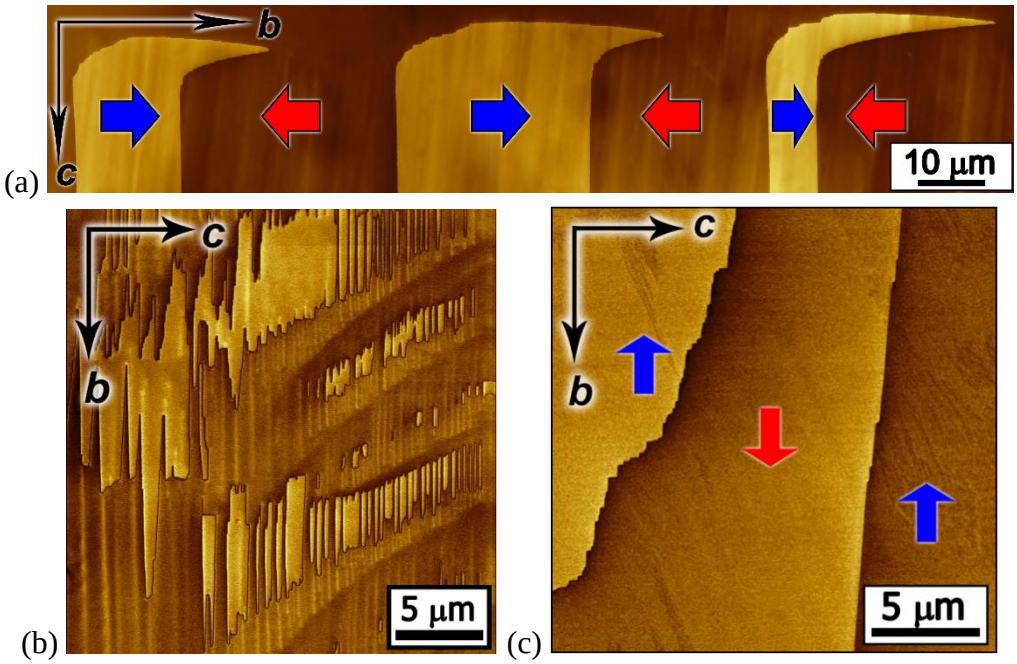

Figure 1. PFM images of the as-grown domain structure types: (a) striped domains with flat charged domain walls, (b) quasiperiodic ensembles of submicron width needle domains, (c) large area domains with irregular shaped domain walls.

The detail experimental study of the neutral and charged domain walls in β-glycine crystals was performed by PFM in the faceted single crystals with in-plane polar axis grown from aqueous solution via drop drying on Pt/SiO/Si substrate in air with controlled relative humidity. Three types of as-grown domain structure were found: (1) striped domains with flat charged domain walls, (2) quasiperiodic ensembles of submicron width needle domains, (3) large area domains with irregular shaped domain walls (Fig. 1). The formation of as-grown domain structure with flat charged domain walls and a smooth change in orientation near the crystal edges can be attributed to growth layers located perpendicular to the polar axis and representing a periodic change in the composition or concentration of impurities [5]. The local direction of spontaneous polarization is determined by the sign of composition or concentration gradient, so the domain walls are localized at the places where the gradient sign changes. The formation of two other types of the as-grown domain structure can be attributed to switching the polarization in the striped domains under the

action of the pyroelectric field E_{pyr}, which appears when the temperature of the crystal changes [6].

The two types of charged domain walls written by the probe differ in morphology. The tail-to-tail walls are straight and smooth, while the head-to-head walls are jagged and zigzag-shaped (Fig. 2). The roughness R_a of tail-to-tail walls was about 15 nm, whereas of head-to-head walls – about 200 nm. This fact also confirms the assumption that the charged tail-to-tail walls are conductive, which accelerates the bulk screening of the depolarization fields created by the bound charges, and low conductivity of the head-to-head walls leads to change in shape to reduce the density of bound charges.

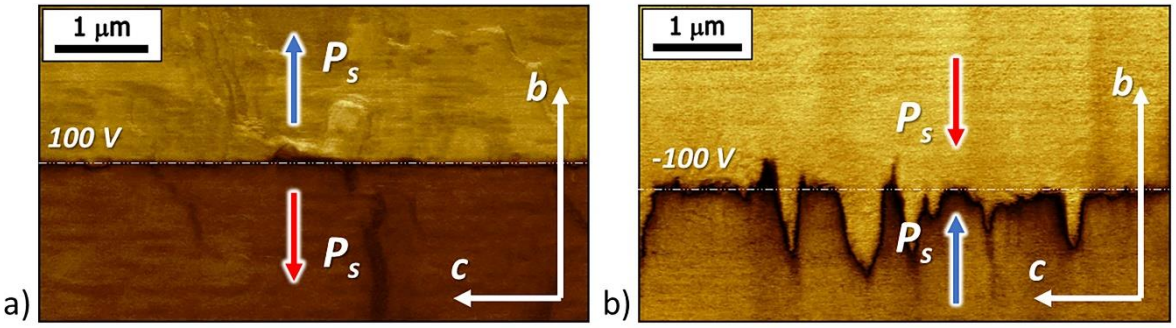

Figure 2. PFM images of the charged domain walls: (a) tail-to-tail and (b) head-to-head. Domain walls were written by local applying of (a) positive (100 V) and (b) negative (-100 V) voltage pulses with duration of 60 s at points located along the straight dotted line with period 1.5 μm.

PFM response at the charged domain walls is perpendicular to the polar axis thus indicating its complex structure. The shallow wells of 0.2-1 nm-depth and about 150 nm-width were revealed along the charged domain walls. The formation of these features was attributed to selective etching by water layer appeared at the crystal surface at the ambient conditions. In contrast the pits appeared at the neutral domain walls are due to deformation of the crystal lattice in the vicinity of the wall.

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